

MD-R103 701

PREPARATION AND CHARACTERIZATION OF MOLECULE-BASED
TRANSISTORS WITH A 50. (U) MASSACHUSETTS INST OF TECH
CAMBRIDGE DEPT OF CHEMISTRY E T JONES ET AL. 03 AUG 87

1/1

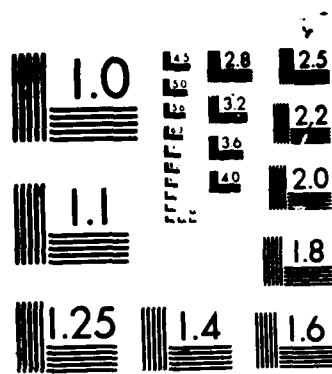
UNCLASSIFIED

TR-17 N00014-84-K-0533

F/G 9/1

NL

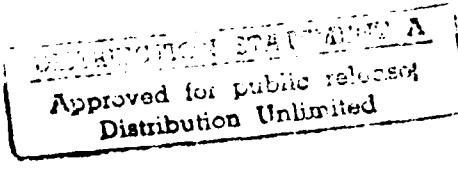
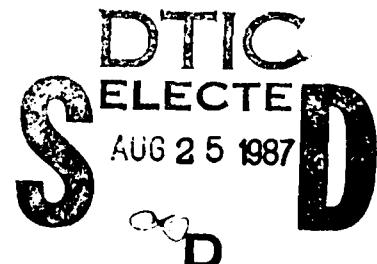




MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

AD-A183 701

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS None	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) No. 17		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) Massachusetts Institute of Technology 77 Mass. Avenue, Bldg. 6-335 Cambridge, MA 02139		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-K-0553	
8c. ADDRESS (City, State, and ZIP Code) Chemistry division 800 N. Quincy Street Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO.	PROJECT NO.
			TASK NO.
			WORK UNIT ACCESSION NO. 051-579
11. TITLE (Include Security Classification) Preparation and Characterization of Molecule-Based Transistors with a 50 Nanometer Source-Drain Separation Using Shadow Deposition Techniques: Towards Faster, More Sensitive.....			
12. PERSONAL AUTHOR(S) E. Tracy Turner Jones, Oliver M. Chyan, Mark S. Wrighton			
13a. TYPE OF REPORT technical interim	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day) August 5, 1987	15. PAGE COUNT 15
16. SUPPLEMENTARY NOTATION Prepared for publication in the Journal of the American Chemical Society			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) microelectrode arrays, polyaniline, Shadow deposition	
FIELD	GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
See Attached Sheet			
 Approved for public release Distribution Unlimited		 S E L E C T E D AUG 25 1987 D D	
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unlimited	
22a. NAME OF RESPONSIBLE INDIVIDUAL Mark S. Wrighton		22b. TELEPHONE (Include Area Code) 617-253-1597	22c. OFFICE SYMBOL

OFFICE OF NAVAL RESEARCH

Contract N00014-84-K-0553

Task No. 051-579

TECHNICAL REPORT NO. 17

Preparation and Characterization of Molecule-Based Transistors
with a 50 Nanometer Source-Drain Separation Using Shadow Deposition
Techniques: Towards Faster, More Sensitive Molecule-Based Devices

by

E. Tracy Turner Jones, Oliver M. Chyan, and Mark S. Wrighton

Prepared for Publication

in

Journal of the American Chemical Society

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

August 5, 1987

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Journal	<input type="checkbox"/>
By	
Date	
Avail Date	
Def	
A-1	

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

Abstract

Preparation of Au microelectrode arrays having spacings of 50-100 nm and available electrode areas of $<10^{-7}$ cm² is described. The dimensions are qualitatively smaller than previously reported and lead directly to faster switching and smaller switching energy for molecule-based transistors. Such microelectrodes can be functionalized with redox active polymers by oxidation of aniline to give polyaniline or by electrochemically assisted deposition of N,N'-bis(p-trimethoxysilylbenzyl)-4,4'-bipyridinium promoting Si-OMe hydrolysis to give the redox polymer (BPQ^{2+/+})_n. The fabrication procedure begins with a microelectrode array consisting of eight, individually addressable Au microelectrodes each \sim 50 μ m long \times \sim 2.5 μ m wide \times \sim 0.1 μ m thick with a spacing of \sim 1.5 μ m between the microelectrodes. A line of sight e⁻ beam deposition of \sim 50 nm of Au at a given angle, using the 0.1 μ m thick microelectrodes to cast a shadow, can be used to close the spacing between microelectrodes to \sim 50 nm. A second line of sight deposition process at a slightly different angle, coats all but a small fraction of the Au with \sim 100 nm of insulating SiO₂ to give ultrasmall Au electrode areas. Molecule-based transistors using polyaniline or (BPQ^{2+/+})_n as the channel material and a pair of microelectrodes as source and drain show that superior speed and sensitivity are the result of the ultrasmall electrode spacings and areas. The dimensions of the channel and the characteristics of the device are consistent with an amount of redox polymer corresponding to \sim 10⁻¹⁴ moles of monomer, a factor of 10² less than used in previously reported molecule-based devices. The devices respond to a small fraction of a femtomole of e⁻'s (10^{-10} C).

[Prepared for publication as a Communication to the Editor of the
Journal of the American Chemical Society]

PREPARATION AND CHARACTERIZATION OF MOLECULE-BASED TRANSISTORS
WITH A 50 NANOMETER SOURCE-DRAIN SEPARATION USING SHADOW DEPOSITION
TECHNIQUES: TOWARDS FASTER, MORE SENSITIVE MOLECULE-BASED DEVICES

E. Tracy Turner Jones, Oliver M. Chyan, Mark S. Wrighton*

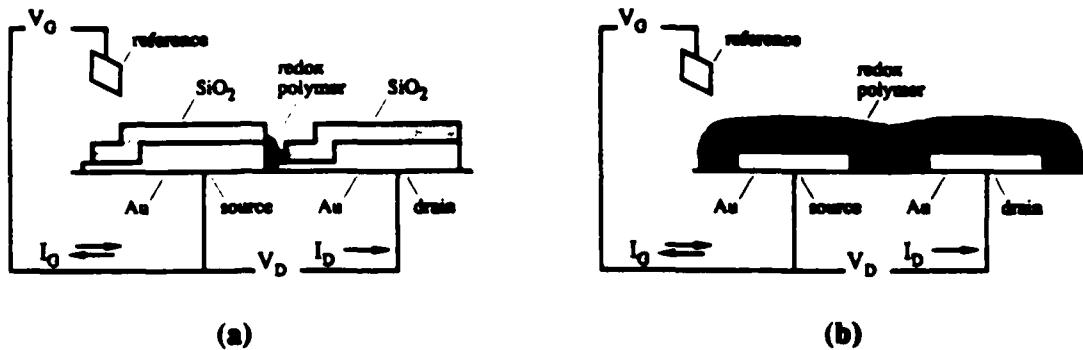
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

*Address correspondence to this author.

Abstract

Preparation of Au microelectrode arrays having spacings of 50-100 nm and available electrode areas of $<10^{-7}$ cm² is described. The dimensions are qualitatively smaller than previously reported and lead directly to faster switching and smaller switching energy for molecule-based transistors. Such microelectrodes can be functionalized with redox active polymers by oxidation of aniline to give polyaniline or by electrochemically assisted deposition of N,N' -bis(*p*-trimethoxysilylbenzyl)-4,4'-bipyridinium promoting Si-OMe hydrolysis to give the redox polymer $(BPQ^{2+/+})_n$. The fabrication procedure begins with a microelectrode array consisting of eight, individually addressable Au microelectrodes each ~ 50 μ m long \times ~ 2.5 μ m wide \times ~ 0.1 μ m thick with a spacing of ~ 1.5 μ m between the microelectrodes. A line of sight e⁻ beam deposition of ~ 50 nm of Au at a given angle, using the 0.1 μ m thick microelectrodes to cast a shadow, can be used to close the spacing between microelectrodes to ~ 50 nm. A second line of sight deposition process at a slightly different angle, coats all but a small fraction of the Au with ~ 100 nm of insulating SiO₂ to give ultrasmall Au electrode areas. Molecule-based transistors using polyaniline or $(BPQ^{2+/+})_n$ as the channel material and a pair of microelectrodes as source and drain show that superior speed and sensitivity are the result of the ultrasmall electrode spacings and areas. The dimensions of the channel and the characteristics of the device are consistent with an amount of redox polymer corresponding to $\sim 10^{-14}$ moles of monomer, a factor of 10² less than used in previously reported molecule-based devices. The devices respond to a small fraction of a femtomole of e⁻'s (10⁻¹⁰ C).

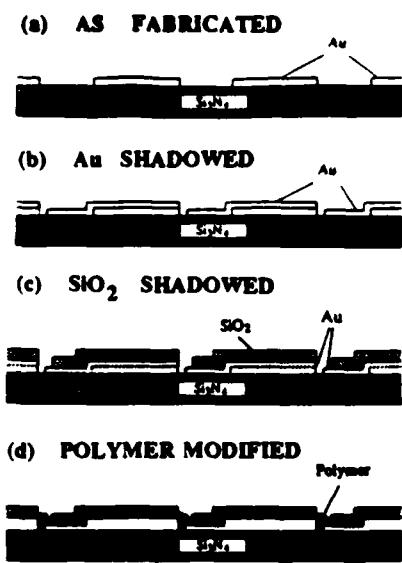
We report preparation and characterization of the molecule-based transistor in Scheme Ia having a significantly smaller (~50 nm vs. 1.5 μ m) source-drain separation and smaller (10^{-14} moles vs. 10^{-12} moles) amount of redox polymer comprising the channel compared to previously reported¹ devices like that in Scheme Ib. The new microstructure with 50 nm source-



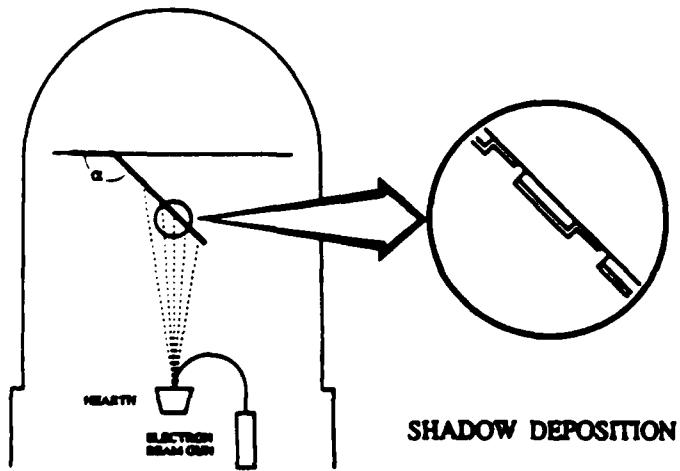
Scheme I (a) Device structure reported here and (b) previously.^{1d}

drain spacing can be prepared by shadow deposition techniques² avoiding need for X-ray³ or e^- beam⁴ lithography. The 50 nm spacing for the open-faced sandwich structure rivals the smallest spacing achievable with conventional sandwich arrangements of electrode/polymer/electrode used to demonstrate the first "bilayer" assemblies.⁵

Scheme II shows the sequence used to prepare the new microstructure Scheme Ia. The procedure begins with a Si_3N_4 -coated Si wafer of microelectrode arrays previously described.^{1a} Each chip on the wafer consists of eight, individually addressable Au microelectrodes each $\sim 50 \mu\text{m}$ long $\times 2.5 \mu\text{m}$ wide $\times 0.1 \mu\text{m}$ thick with spacings between microelectrodes of $\sim 1.5 \mu\text{m}$. The first step involves a line of sight e^- beam deposition of 50 nm of Au onto the wafer at an angle α as illustrated in Scheme III. Generally, prior



Scheme II. Fabrication sequence
for a 50 nm device.



Scheme III. Shadow deposition
apparatus.

to Au deposition 5 nm of Cr is deposited as an adhesion layer. The line of sight deposition of Au results in a larger ($\sim 4 \mu\text{m}$ wide) microelectrode than the original ($2.5 \mu\text{m}$ wide) but the spacing can be closed to 50 to 100 nm as established by scanning electron microscopy (SEM), Figure 1. Variation of α gives rise to variation in the spacing in a manner consistent with the length of the expected shadow. From SEM it is evident that imperfections on the edges of the original microelectrodes give rise to uneven spacings between the microelectrodes after shadow deposition. Indeed, the shadows accurately "image" the imperfections in a straightforward manner. Spacings cited here are "average" values.

The larger microelectrodes formed by shadow deposition of Au have the disadvantage that the absolute amount of electroactive area is relatively large. When redox material is electrochemically deposited, a device results that involves a much larger amount of active material than required to span the

50 nm spacing. A second shadow deposition process, Scheme II, line of sight e- beam deposition of 100 nm of SiO₂ at an angle = smaller than for the Au deposition step, covers the majority of the exposed Au with an insulator, Figure 1. The result is a set of closely-spaced (50-100 nm) microelectrodes with ultrasmall electrode areas. The total microelectrode area available depends on the original microelectrode thickness, \propto for SiO₂ deposition, and the thickness of the shadow deposited Au. Typical area available is estimated to be below 10⁻⁷ cm² per microelectrode. Figure 1 includes SEM showing a closely-spaced pair of microelectrodes that are the product of the shadow deposition of Au followed by SiO₂. Electrochemical deposition of (BPQ^{2+/-})_n,⁶ from N,N'-bis(p-trimethoxysilylbenzyl)-4,4'-bipyridinium, or polyaniline^{1d,7} onto the microfabricated structure shows that the SiO₂ is an effective insulator and that the exposed Au is electrochemically active. SEM establishes polymer to be deposited mainly in the 50 nm channel region as in Scheme Ia. Electrochemical characterization of the system shows that the amount of polymer needed to make a connection is <10⁻¹⁴ moles of BPQ²⁺ units as established by the integration of a cyclic voltammogram associated with the BPQ²⁺ \leftrightarrow BPQ⁺ interconversion for microelectrodes connected by the (BPQ^{2+/-})_n polymer. These data show that 10⁻² times the amount of (BPQ^{2+/-})_n is needed in comparison to the original microelectrode array.

Smaller microelectrode spacing and smaller polymer volume mean that molecule-based transistors require less energy for switching and can be switched more rapidly.^{1d} Polyaniline-based transistors, Scheme Ia, with 50-100 nm source-drain separation have been demonstrated to switch from off to maximum on by passing <10⁻⁹ C, 10⁻² times the charge needed with the original dimensions.^{1d} Figure 2 includes an electrochemical characterization of the polyaniline connecting two microelectrodes in that the IG vs. VG is in essence a cyclic

voltammogram with a sinusoidal variation in voltage. Figure 2 also reveals the change in conductivity accompanying cyclic oxidation/reduction as reflected in variation in I_D as V_G is varied. The data demonstrate power gain at frequencies exceeding 10 kHz almost 10^2 times higher than for a control device with a $1.5 \mu\text{m}$ 10 kHz the device turns on to nearly the same extent as at 1 Hz. The polyaniline device shows an easily detected variation in drain current, I_D , for flow of only 10^{-12} C in the gate circuit accompanying ΔV_G in the V_G region of maximum transconductance. Thus, the device can respond to a small fraction of a femtomole (10^{-10} C) of charge.

Acknowledgements We thank the Office of Naval Research and the Defense Advanced Research Project Agency for partial support of the research. Use of the facilities in the M.I.T. Microsystems Technology Laboratories and the NSF-supported Materials Research Laboratory is also gratefully acknowledged.

References

1. (a) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. J. Am. Chem. Soc., 1984, 106, 7389; (b) Paul, E. W.; Ricco, A. J.; Wrighton, M. S. J. Phys. Chem., 1985, 89, 1441; (c) Thackeray, J. W.; White, H. S.; Wrighton, M. S. J. Phys. Chem., 1985, 89, 5133; (d) Lofton, E. P.; Thackeray, J. W.; Wrighton, M. S. J. Phys. Chem., 1986, 90, 6080.
2. (a) Dean, R. H.; Matarese, R. J. IEEE Trans. Electron Devices, 1975, ED-22, 358; (b) Dolan, G. J. Appl. Phys. Lett., 1977, 31, 337; (c) Speidell, J. L. J. Vac. Sci. Technol., 1981, 19, 693; (d) Holdeman, L. B.; Barber, R. C.; Abita, J. L. J. Vac. Sci. Technol., 1985, B3, 956.
3. (a) Flanders, D. C. Appl. Phys. Lett., 1980, 36, 93; (b) Chou, S. Y.; Smith, H. I.; Antoniadiis, D. A. J. Vac. Sci. Technol., 1985, B3, 1587; (c) Smith, H. I. J. Vac. Sci. Technol., 1986, B4, 148.
4. (a) Crewe, A. V. J. Vac. Sci. Technol., 1979, 16, 255; (b) Howard, R. E.; Hu, E. L.; Jackel, L. D.; Grabbe, P.; Tennant, D. M. Appl. Phys. Lett., 1980, 36, 592; (c) Dix, C.; Flavin, P. G.; Hendy, P.; Jones, M. E. J. Vac. Sci. Technol., 1985, B3, 131; (d) Emoto, F.; Gamo, K.; Namba, S.; Samoto, N.; Shimizu, R. Jpn. J. Appl. Phys., 1985, 24, L809.
5. (a) Pickup, P. G.; Murray, R. W. J. Am. Chem. Soc., 1983, 105, 4510; (b) Pickup, P. G.; Leidner, C. R.; Denisevich, P.; Murray, R. W. J. Electroanal. Chem., 1984, 164, 39; (c) Pickup, P. G.; Kutner, W.; Leidner, C. R.; Murray, R. W. J. Am. Chem. Soc., 1984, 106, 1991; (d) Morishima, Y.; Fukushima, Y.; Nozakura, S. J. Chem. Soc., Chem. Commun., 1985, 13, 912; (e) Elliott, C. M.; Redepenning, J. G.; Balk, E. M., J. Electroanal. Chem. 1986, 213(2), 203; (f) Chidsey, C. E. D.; Murray, R. W. Science, 1986, 231, 25.

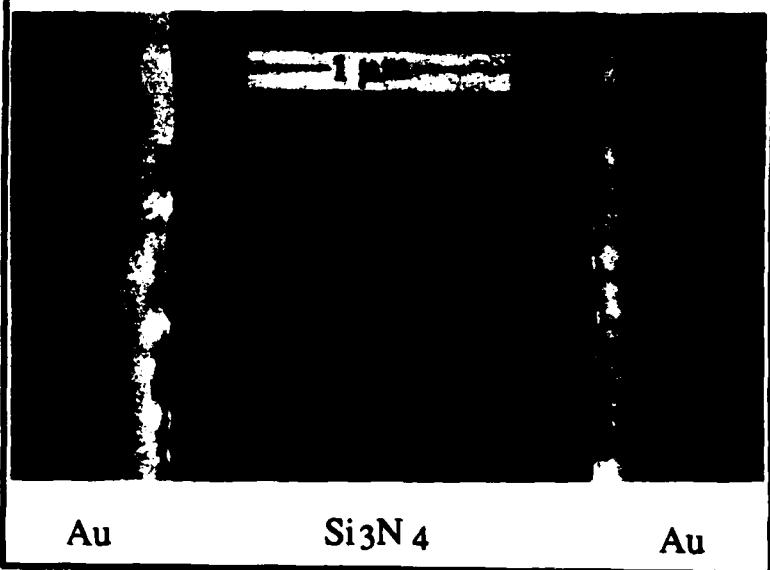
6. (a) Dominey, R. N.; Lewis, T. J.; Wrighton, M. S. J. Phys. Chem., 1983, 87, 5345; (b) Lewis, T. J.; White, H. S.; Wrighton, M. S. J. Am. Chem. Soc., 1984, 106, 6947.
7. (a) Mohilner, D. M.; Adams, R. N.; Argersinger, T. W. J. Am. Chem. Soc., 1962, 84, 3618; (b) Jozefowicz, M.; Yu, L. T.; Perichon, J.; Buvet, R. J. Polym. Sci., Part C, 1969, 22, 1187; (c) Diaz, A. F.; Logan, J. A. J. Electroanal. Chem., 1980, 111, 111.

Figures

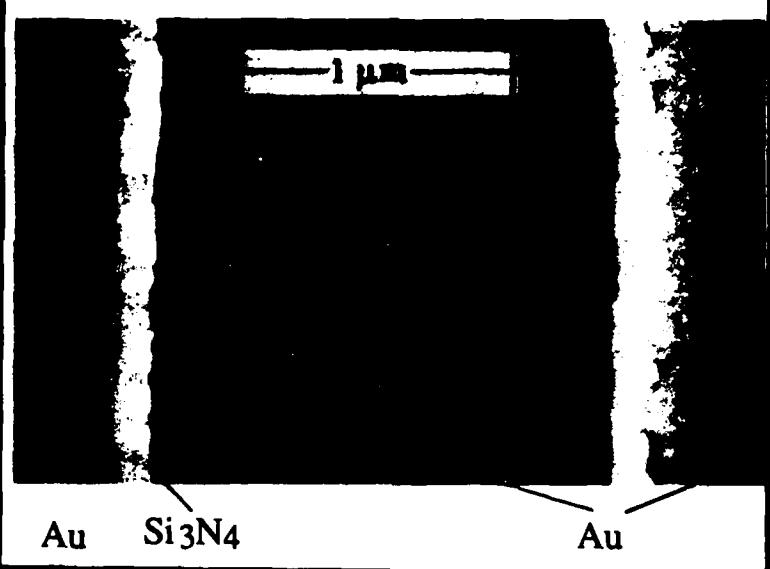
Figure 1. Scanning electron micrographs of a pair of microelectrodes at different stages of the fabrication sequence, Scheme II. (a) Original microelectrodes with 1.5 μm spacing. (b) Gap closed to 50-70 nm by shadow deposition of Cr and Au. (c) Electroactive area of previously widened microelectrodes reduced upon shadow deposition of insulating SiO_2 layer. Uneven spacing reflects original imperfections on the edge of the left microelectrode.

Figure 2. Gate potential (V_G), gate current (I_G), and drain current (I_D) at 10 kHz for an ultrasmall gap polyaniline-based transistor, drain voltage $V_D = 100$ mV. Inset shows \log_{10} (amplification) vs. \log_{10} (frequency) of 1.5 μm gap () vs. 70 nm gap () polyaniline-based transistor, Scheme I. Blank experiments (no polyaniline on microelectrodes) show that the I_G and I_D measured for the polyaniline-based device are principally (>99 %) due to oxidation/reduction and resulting changes in conductivity of polyaniline

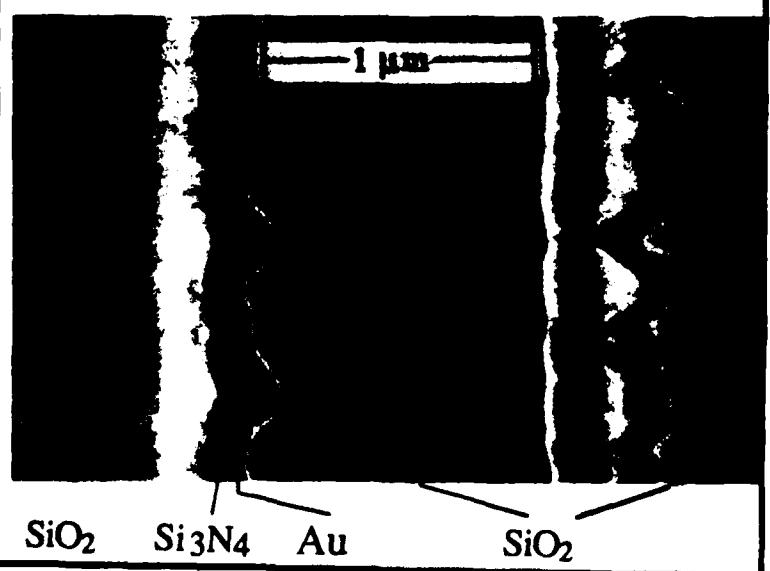
(a) AS FABRICATED

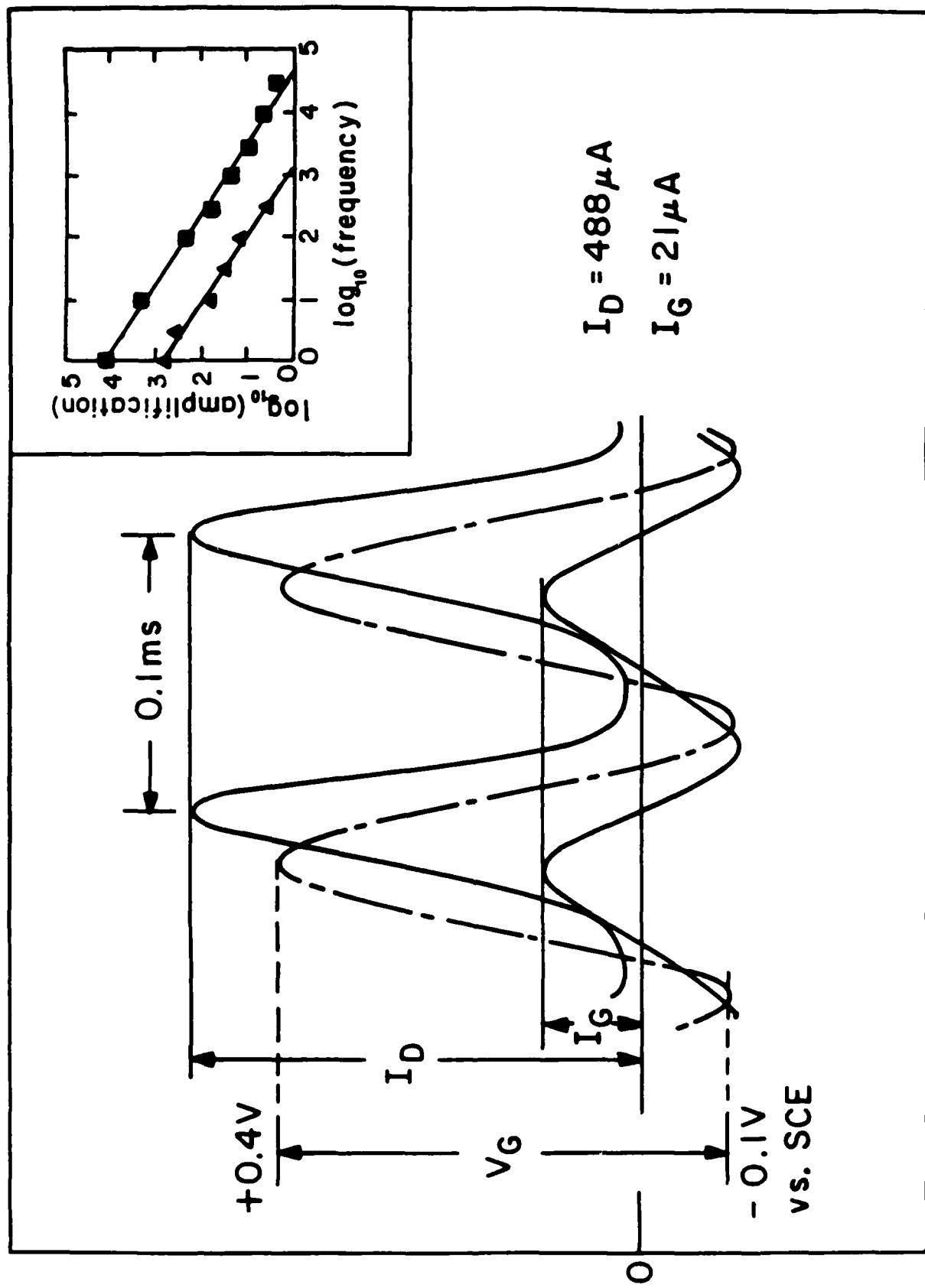


(b) Au SHADOWED



(c) SiO_2 SHADOWED





01/11/87/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

9-87

DTIC